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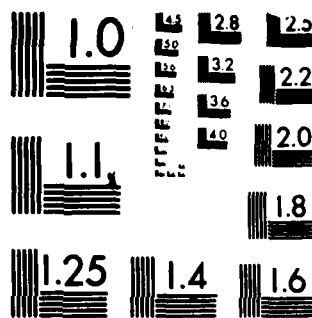
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D. R. Sandstrom, E. C. Marques, and R. E. Hamm

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Cl K-edge X-ray absorption spectra were measured for concentrated ferric chloride solutions. A single pre-edge XANES feature due to transitions to metal 3d derived orbitals depends on concentration according to the degree of direct Fe ²⁺ -Cl ⁻ bonding. Fourier transformed EXAFS spectra show well separated contributions due to Fe and O backscatterers.		

Cl K-EDGE X-RAY ABSORPTION STUDIES OF CONCENTRATED
FERRIC CHLORIDE SOLUTIONS

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Special techniques have been developed to measure X-ray absorption spectra in the vicinity of the Cl K-edge (2822.4 eV) using a focused synchrotron radiation source (SSRL beam line II-3). Features of the technique include (a) fluorescence detection of characteristic Cl secondary emission using an N₂ filled ion chamber detector; (b) detuning of monochromator crystal parallelism to reduce third harmonic content in the incident beam (second harmonic was already absent for the Si(111) monochromator crystals used); and (c) use of a helium filled beam transmission path for the in-hutch portion of the experiment. Because of the large Bragg angle for the Cl K-edge [44.47° for Si(111)], the resolution of even the focused beam line was sufficient to measure both XANES and EXAFS. It is estimated that the resolution of beam line II-3 is better than 1 eV at the Cl K-edge.

Hydrated FeCl₃ crystals and aqueous solutions of FeCl₃ having concentrations ranging from 0.40 to 5.75 moles/liter were investigated, along with a series of other transition metal salts and solutions.

Both the XANES and EXAFS spectral regions provide significant detail about structure in the FeCl₃ solutions. In the XANES region, a single pre-edge peak is present for the solid hydrated FeCl₃ salt, all the FeCl₃ solutions, and some other transition metal chloride solid salts and solutions. The same feature is consistently absent from spectra for alkali and alkaline earth metal chloride solid salts and solutions. This pre-edge feature of the XANES spectrum is understood on the basis of previous studies of Cl K-edge absorption spectra for solid transition metal chlorides [1] to be due to transitions from the Cl 1s level to molecular orbitals derived from the metal 3d state. By extending such studies to FeCl₃ and other transition metal solutions, the present work demonstrates that this transition also occurs for transition metal chloride complexes in solution. For the series of FeCl₃ solutions, the magnitude of the pre-edge transition, relative to the absorption edge jump, was observed to increase with increasing concentration, in accord with an expected increase [2] in the fraction of chloride ions participating in direct Fe²⁺-Cl⁻ bonding at higher concentration. The XANES spectrum at the Cl K-edge for these

solutions contrasts markedly with that measured at the Fe K-edge in that the latter shows only a very weak pre-edge peak. In this respect, Cl K-edge XANES spectra show a dramatic advantage as an indicator of direct metal-chloride bonding in solution.

EXAFS spectra measured at the Cl K-edge also exhibit considerable structural detail. Both Fe and O backscatterers contribute significantly to the observed oscillations, but these effects are well separated in the Fourier transforms of the EXAFS spectra, because of the large difference in bond length for the Fe and O neighbors. In this respect, interpretation of the Cl K-edge spectra is more straightforward than are those of Fe K-edges because of overlap in the Fourier transform between the Fe-Cl and Fe-O contributions to the EXAFS oscillations. Fourier transforms of the present Cl K-edge EXAFS data clearly show a concentration dependent increase in the relative degree of Cl-Fe bonding, and a corresponding decrease on the Cl-O coordination.

By extending applicability of x-ray absorption spectroscopy to both anion and cation species in chloride solutions, the present work opens up the possibility of a full description of speciation comparable to that of previous work on bromide solutions. [3]

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